(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 254 366 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:
11.05.2005 Bulletin 2005/19

(21) Application number: **01907053.1**

(22) Date of filing: **07.02.2001**

(51) Int Cl.[7]: **G01N 27/49**, A61L 2/24

(86) International application number:
PCT/US2001/003885

(87) International publication number:
WO 2001/057513 (09.08.2001 Gazette 2001/32)

(54) **ELECTROCHEMICAL SENSOR FOR THE SPECIFIC DETECTION OF PERACETIC ACID IN AQUEOUS SOLUTIONS USING PULSE AMPEROMETRIC METHODS**

ELEKTROCHEMISCHER SENSOR ZUR BESTIMMUNG VON PERESSIGSÄURE IN WÄSSERIGEN LÖSUNGEN MITTELS PULSAMPEROMETRISCHEN-VERFAHREN

DETECTEUR ELECTROCHIMIQUE POUR LA DETECTION SPÉCIFIQUE D'ACIDE PERACETIQUE DANS DES SOLUTIONS AQUEUSES UTILISANT DES METHODES AMPEROMETRIQUES PULSEES

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE TR

(30) Priority: **07.02.2000 US 499421**

(43) Date of publication of application:
06.11.2002 Bulletin 2002/45

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Description

Background of the Invention

[0001] The present invention relates to the sterilization and disinfection arts. It finds particular application in conjunction with the detection of peracetic acid concentrations in solutions used for sterilization or disinfection of medical, dental, and pharmaceutical equipment and will be described with particular reference thereto. It should be appreciated, however, that the invention is also applicable to detection of peracetic acid and other oxidizable chemicals, such as hydrogen peroxide, in solution.

[0002] Peroxyacetic acid, or peracetic acid, is a useful sterilant and/or disinfectant for a variety of applications, including disinfection of waste and sterilization or disinfection of medical, dental, pharmaceutical, or mortuary equipment, packaging containers, food processing equipment, and the like. It has a broad spectrum of activity against microorganisms, and is effective even at low temperatures. It poses few, if any, disposal problems because it decomposes to compounds which are readily degraded in sewage treatment plants. Peracetic acid solutions also have the ability to be reused over a period of time, allowing instruments to be sterilized or disinfected throughout the day in the same bath of sterilant.

[0003] In use, peracetic acid precursors are typically mixed with water and other chemicals in order to create a sterilant solution. Items to be sterilized or disinfected are then immersed in the sterilant. Decontaminated items are then rinsed to remove traces of the acid and other cleaning chemicals, before use. To ensure effective sterilization or disinfection within a preselected period of time, the concentration of peracetic acid is maintained above a selected minimum effective level. Disinfection is typically carried out at lower concentrations of peracetic acid than for sterilization. When the peracetic acid concentration is at or above the minimum effective level, complete sterilization or disinfection is expected.

[0004] Because the peracetic acid tends to decompose over time, it is valuable to monitor the sterilant periodically to determine the level of peracetic acid. The level can be compared against preselected minimum levels, used to adjust contact time, used to control concentration, or the like. Currently, it is often assumed that the sterilant will remain at or above the minimum effective concentration. However, differences in the temperature of the sterilant, the quantity of items sterilized or disinfected, and the degree and nature of contamination of the items all result in considerable variations in the degradation of the sterilant. In addition, storage conditions and duration sometimes lead to degradation of the peracetic acid precursors before use.

[0005] Methods currently used to detect peracetic acid are often unable to distinguish between peracetic acid and other compounds typically present in the solution, such as hydrogen peroxide and acetic acid. Dippable papers are easy to use, but lack accuracy, particularly at concentrations suitable for sterilization or disinfection. Chemical titration methods provide a more accurate measure of the peracetic acid in solution, but are time consuming to perform and are not readily automated. Frequently, more than one titration is performed to eliminate the contribution of hydrogen peroxide to the result.

[0006] Recently, a number of electrochemical techniques have been developed for detection of oxidizable or reducible chemical species, such as peracetic acid. Consentino, et al., U.S. Patent No. 5,400,818, discloses a sensor for peracetic acid-hydrogen peroxide solutions. The sensor measures the resistivity of the solution, which is dependent on both the peracetic acid and the hydrogen peroxide concentrations, as well as other factors. Thus, the sensor is unable to differentiate between the two components.

[0007] European Patent Application EP 0 333 246 A, to Unilever PLC, discloses an electrochemical sensor for detection of oxidizable or reducible chemical species using an amperometric method in which a fixed potential is maintained between a reference and a working electrode. The current at the working electrode is used to determine the concentration of peracetic acid. Other species present, however, influence the current flowing, and hence the accuracy of the results.

[0008] Teske, U.S. Patent No. 5,503,720, discloses a process for the determination of reducible or oxidizable substances, such as peracetic acid in sewage waste. The process uses potentiostatic amperometry to detect peracetic acid concentrations. The technique, however, depends on the achievement of a steady state, which frequently takes several hours.

[0009] DE 44 12576 to Henkel discloses a process for amperometric determination of peracetic acid in a laundry bath. Pulsed amperometry is used to clean a gold working electrode between peracetic acid measurements, which are carried out by precipitation of peracetic acid at the working electrode.

[0010] U.S. 5,873,990 discloses a handheld device for measurement of heavy metal ions and other species in blood. Amperometric measurements of hydrogen peroxide are made with a colloidal gold/peroxidase sensor while square wave voltammetry and a carbon electrode are used for monitoring acetaminophen.

[0011] Conventional electrochemical detection systems often employ a porous membrane, which separates the sample to be analyzed from the electrodes. Species to be measured pass through the membrane when traveling to the electrodes. This increases the time for measurements to be made and adds complexity and cost to the system.

[0012] The present invention provides a new and improved method for the selective detection of peracetic acid, which overcomes the above-referenced problems and others.

Summary of the Invention

[0013] In accordance with one aspect of the present invention, a method of detecting peracetic acid in a solution which also contains hydrogen peroxide is provided. The method comprises disposing a carbon working electrode, a reference electrode, and optionally a counter electrode in the solution to be tested, selectively pulsing a read voltage to the working electrode, and detecting current flowing between either the working electrode and the reference electrode or the working electrode the counter electrode, where present. The read voltage is selected such that the current flowing is dependent on a concentration of peracetic acid and substantially independent of a concentration of the hydrogen peroxide in the solution and is in the range of -0.5 to -1.4 volts, relative to a silver/silver chloride reference electrode. The detected current flow is converted into an indication of the concentration of the peracetic acid in the solution.

[0014] One advantage of one embodiment of the present invention is that it enables the peracetic acid concentration of a sterilizing or disinfecting solution to be determined rapidly, (i.e., in less than one minute) and without interference by other oxidizing species present in the solution.

[0015] Another advantage of one embodiment of the present invention is that a minimum effective concentration of peracetic acid is maintained for effective sterilization or disinfection.

[0016] Still further advantages of the present invention will become apparent to those of ordinary skill in the art upon reading and understanding the following detailed description of the preferred embodiments.

Brief Description of the Drawings

[0017] The invention may take form in various components and arrangements of components, and in various steps and arrangements of steps. The drawings are only for purposes of illustrating a preferred embodiment and are not to be construed as limiting the invention.

FIGURE 1 is a plumbing diagram of a peracetic acid sterilization and disinfection system for use in the present invention;

FIGURE 2 is a schematic diagram of an electrochemical system for detecting peracetic acid using pulse amperometry according to the present invention;

FIGURE 3 is a top view of a disposable sensor for detecting peracetic acid for use in the present invention;

FIGURE 4 is a side view of a reusable sensor system, for use in the present invention;

FIGURE 5 is a side view through section V-V of the reusable sensor system of FIGURE 4;

FIGURE 6 is a plot showing a pulse sequence applied between reference and working electrodes of the sensor system of FIGURE 1;

FIGURE 7 is a plot showing cyclic voltammograms of current flow against electrode voltage for solutions containing (1) a buffering system, (2) a buffering system and 1500 ppm peracetic acid, and (3) a buffering system and 500 ppm hydrogen peroxide and peroxide ions, for a pyrolytic graphite working electrode;

FIGURE 8 is a plot showing cyclic voltammograms in peracetic acid solutions at different concentrations using a glassy carbon electrode; and

FIGURE 9 is a plot showing cyclic voltammograms in peracetic acid solutions at different concentrations using a pyrolytic graphite carbon electrode.

Detailed Description of the Preferred Embodiments

[0018] With reference to FIGURE 1, a peracetic acid monitoring system or sensor A measures peracetic acid concentrations in the presence of hydrogen peroxide. The monitoring system will be described with reference to an automated liquid decontamination apparatus **1** which sequentially cleans items, such as endoscopes or other medical, dental, and pharmaceutical devices, and the like, and then sanitizes, sterilizes, or disinfects them with a decontaminant solution which contains peracetic acid. It should be appreciated, however that the monitoring system is also applicable to the measurement of peracetic acid concentrations in other treatment systems and peracetic acid-containing liquids.

[0019] The term "decontamination" and other terms relating to decontaminating will be used herein to describe sanitizing, sterilization, disinfection, and other antimicrobial treatments which are designed to destroy microorganisms contaminating the items.

[0020] The system **1** includes a decontamination cabinet **10** which defines an interior decontamination chamber **12.** Items to be sterilized, disinfected, sanitized, or otherwise microbially decontaminated are loaded into the decontamination chamber through an opening in a front wall **13** of the cabinet, illustrated as closed by a door **14.** Within the chamber, several spray jets or nozzles **16** spray a decontaminant solution over the items. Optionally, in the case of instruments with lumens, or other internal passages, some of the nozzles act as fluid ports **18** which are configured for interconnection with internal passages of the endoscopes and other objects with lumens, for supplying decontaminant solution and other liquids to the internal passages.

[0021] A collection tank or sump **20** forms the base of the cabinet **10** and receives the sprayed decontaminant solution as it drips off the items. A high pressure pump **22** delivers the decontaminant solution under pressure to the nozzles **16** and fluid ports **18** through a fluid distribution system or manifold **24.**

[0022] A source **30** of a decontaminant solution preferably includes a well or mixing chamber **34.** The well receives a dose of a concentrated decontaminant, such

as an antimicrobial agent or reagents which react to form an antimicrobial agent on mixing with water. As shown in FIGURE 1, the well is preferably integral with the collection tank **20** of the chamber, although a separate well is also contemplated.

[0023] A preferred antimicrobial agent is peracetic acid, either in concentrated liquid form, or as a reaction product of powdered reagents, such as acetyl salicylic acid and sodium perborate. A water inlet **42** supplies water, typically from a municipal water system to the well. The water mixes with detergents, corrosion inhibitors, the concentrated decontaminant, and other selected components in the well to form wash, decontaminant, or other solutions.

[0024] Preferably, the concentrated decontaminant and the other components are supplied in a disposable package or cup **44** which is positioned in the well **34** prior to a decontamination cycle. The cup **44** holds a measured dose of the concentrated decontaminant. Optionally, a cleaner concentrate is also contained in the cup for forming a cleaning solution to clean the items prior to antimicrobial decontamination. The cup **44** may include a number of compartments which separately contain the cleaning concentrate and decontaminant concentrate for separate release into the system. In this way, the items are first cleaned and then microbially decontaminated.

[0025] In a preferred embodiment, the cup holds a cleaning concentrate in a first compartment. A second compartment holds pretreatment components, such as buffers for adjusting the pH, surfactants, chelating agents, and corrosion inhibitors for protecting the components of the system and items to be decontaminated from corrosion by the decontaminant. A decontaminant, such as concentrated liquid peracetic acid solution (or reagents that react to form it) is held in a third compartment. A cup cutter **46**, or other suitable opening member, is positioned at the base of the well **34** for opening selected compartments of the cup, in sequence.

[0026] Alternatively, a solid or liquid concentrated decontaminant is supplied to the system from a separate bulk source (not Shown), or is supplied to the system as the decontaminant solution, in an already-diluted form.

[0027] The water used for diluting the cleaner concentrate and decontaminant may be tap water or treated water, such as distilled water, filtered water, microbe free water, or the like. The quantity of water entering the system is regulated to provide a decontaminant solution of a desired concentration in the decontamination chamber **12**. The water is preferably passed through a microporous filter **50** in the water inlet line **42** which filters out particles of dirt and microorganisms. A valve **52** in the water inlet **42** closes when the selected quantity of water has been admitted.

[0028] A fluid supply pathway **60** connects the well **40**, the pump **22**, and the fluid distribution system **24**. A heater **64**, situated in the fluid supply pathway **60**, heats the decontaminant solution and optionally the cleaning solution and rinse liquid to a preferred temperature(s) for effective cleaning, decontamination, and rinsing. A temperature of about 50-60°C is preferred for sterilization with peracetic acid. The pathway **60** returns the sprayed decontaminant solution from the sump **20** to the manifold **24**, and thence to the nozzles **16** and the fluid ports **18** via a recirculation valve **68**. At least a portion of the sprayed decontaminant solution is directed through the well **34** before being returned to the decontamination chamber. This ensures thorough mixing of the concentrated decontaminant and other components with the solution before returning the decontaminant solution to the nozzles **16, 18**.

[0029] The peracetic acid monitoring system **A** detects the concentration of peracetic acid passing through the fluid lines. FIGURE **1** shows the system connected with the line **60**. It should be appreciated, however, that the sensor is also conveniently connected with or disposed in any of the fluid flow lines of the system or simply in a bath of decontaminant solution. A computer control system **80** controls the operation of the peracetic acid monitoring system A. Preferably, the control system also controls the operation of other elements of the system **1**, including the introduction of the cleaner concentrate, the peroxy concentrate, and other reagents as well as the pump **22**, the heater **64**, the valves **52, 68** and the like. The control system **80** may control one or more additional systems **1**, if desired.

[0030] With reference now to FIGURE 2, the system **A** for selective detection of peracetic acid includes an electrode system **110**, and an amperometric controller **112**. The controller **112** both applies voltages and detects current flows in the system A. Although the controller is shown as a single unit in FIGURE 2, it should be understood that a combination of pieces of electrochemical equipment generally known in the art which serves these functions is also contemplated.

[0031] The electrode system **110** is disposed in a reservoir **114** which receives a peracetic acid solution to be tested, or may be placed directly in the recirculation path of the automated processor 1. Preferably, as shown in FIGURE **1**, the reservoir comprises a separate chamber, into which a sample of the circulating decontaminant solution is withdrawn at intervals. Because peracetic acid is generally in equilibrium with hydrogen peroxide when in solution, the solution to be tested invariably contains some hydrogen peroxide.

[0032] The electrode system 110 can be a two or three electrode system. In a three electrode system it includes a working or sensing electrode **118**, a reference electrode 120, and a counter electrode 122. In a two electrode system, the counter electrode is eliminated in favor of a reference electrode which also serves the functions of the counter electrode, although with some loss in stability of the system to be expected.

[0033] The reference electrode produces a constant electrical potential (or base potential) and assures a stable reference potential when the current density flowing

through the electrode is small. Suitable reference electrodes 120 include silver/silver chloride electrodes.

[0034] The working electrode is formed from a carbon material and is an electroactive for peracetic acid. Other features of good working electrode materials include minimal to no consumption of the electrode material during operation of the sensor, useful working potential range covering the detection potential of peracetic acid, provision of a high signal to background noise ratio for peracetic acid, and a low sensitivity to interfering substances, such as hydrogen peroxide. Carbon is an effective electroactive for peracetic acid and is highly selective for peracetic acid in the presence of hydrogen peroxide. Carbon electrodes are also relatively resistant to peracetic acid, giving them a longer useful life. Crystalline forms of carbon, such as graphite, provide effective working electrodes for measurements in the diffusion limited region. One preferred form of crystalline carbon is pyrolytic graphite (obtainable from Advanced Ceramics Corp), a highly crystalline form, manufactured by decomposition of hydrocarbon gas at high temperatures in a vacuum furnace. Another form of crystalline carbon is sold under the tradename Isomolded graphite by Industrial Sales, Melrose Park, Ill. Amorphous forms of carbon, such as glassy carbon, also provide effective working electrode materials for measurements in the diffusion limited region.

[0035] The counter electrode **122**, where used, is preferably formed from an inert conductive material, such as carbon. Alternatively, suitable counter electrodes are formed from silver, gold, platinum, or titanium. The external circuit is closed between the working electrode and the counter electrode.

[0036] With reference to FIGURE 3, in one embodiment, a substrate **124**, preferably formed from an inert polymeric or ceramic sheet, supports the electrode system **110** to form a disposable probe **125**. Electric leads **126** electrically connect the electrodes and the controller **112** through connecting points **128**. Optionally, the sensor probe also includes an insulation layer **130** which covers the substrate and the leads around the connection points. The insulation layer inhibits the leads from participating in the electrochemical reactions. Optionally, a thermistor **132** detects the temperature of the sample in the region around the probe.

[0037] The sensor probe **125** is preferably constructed by photolithographic metalization or thick film printing technology, although other methods of probe formation are also contemplated. In one embodiment, components of the sensor, including electrodes, electrical connection points and electrical leads are all laid down on the substrate.

Materials for the electrodes and connection points are separately dispersed in inks and printed onto the substrate. The inks are cured, for example, by heat, UV light, or the like. The probes produced are inexpensive and thus are suited to single use. Additionally, such probes can be used without prior calibration. The electrode materials are selected so that they will not become disbonded when immersed in a peracetic acid solution at temperatures between around 25°C and 75°C. The choice of ink also affects the conductivity to some degree.

[0038] In another embodiment, shown in FIGURES 4 and 5, where like components are numbered with a prime ('), a sensor **A'** includes a durable, reusable electrode system **110'** is shown. The electrode system **110'** comprises a working electrode **118'**, a reference electrode **120'** and a counter electrode **122'**. The electrodes are analogous to those described above for the disposable sensor, but in this embodiment, are constructed to be reusable. The electrodes are mounted in a housing **150** formed from stainless steel or other material with a large heat capacity.

[0039] The housing **150** defines an interior chamber or reservoir **114'**. Working faces of the three electrodes **118', 120', 122'** project through walls **156** of the housing into the chamber. The electrodes are sheathed with and receive mechanical support from insulating material **158** so that only the working faces are exposed to the peracetic acid sample. Steel tubes **160** are threadably, or otherwise removably attached to the walls of the chamber and carry the electrodes therethrough for ease of insertion and removal of the electrodes from the chamber and for mechanical support exterior to the chamber.

[0040] An inlet line **162** carries a sample of the circulating decontaminant solution into the chamber through an inlet **164** formed in one wall of the housing **150.** A diaphragm valve **168** in the inlet line is normally closed, except when a sample is being taken. An overflow or drain line **170** carries fluid from the chamber via an outlet **172** defined through an opposite wall of the chamber. The overflow line leads to a drain via an inverted U-bend or trap **174** or returns the sample to the fluid flow line **60.** It is preferred to direct the decontaminant solution to drain since this eliminates the need to assure sterility of reservoir surfaces of the sensor housing.

[0041] The chamber **114'** and housing **150** are configured such that the thermal mass of the housing is substantially greater than the volume of the decontaminant solution to be sampled. The internal volume of the chamber is preferably about 10-15 ml or less. One or more thermal elements **176**, within the walls **156** of the housing, maintains the housing at a stable temperature, and thereby the sampled fluid. Preferably, the sample is heated to a measurement temperature only slightly above the maximum temperature expected in the circulating fluid. This allows the sample to reach the measurement temperature very quickly. For example, if the decontamination portion of the cycle operates at about 50-55°C, the walls are preferably maintained at about 60°C. Alternatively, the sample may be cooled by cooling elements, such as by Peltier elements, to achieve an optimum measuring temperature. A thermocouple **132'**, or other temperature detector, detects the temperature of the chamber walls or the sampled fluid in the

chamber. A temperature detector **178** receives signals from the thermocouple and adjusts the thermal elements to maintain the walls at a constant temperature. Alternately, compensation for temperature fluctuations can be made in the calculation of concentration, the currents from the electrodes, or the like. Preferably, the large, heated mass of the housing quickly brings the sample to a reproducible as well as stable temperature.

[0042] When a sample is to be taken, the valve **168** opens and allows the sampled fluid to flow into the chamber. The valve **168** remains open for sufficient time to allow the sampled fluid to flush the contents of the chamber through the overflow and replace the contents with freshly sampled fluid. Alternatively, to conserve fluid, the drain valve may be opened to allow the prior sample to flow from the chamber. The valve is then closed and the chamber filled with a rinsing sample, which may be the same as the measurement sample. The rinsing sample is then drained and the chamber filled with a sample for measurement. In the system **1**, the pump **22** pressurizes the circulating decontaminant to about 70 psi. In this case, a flush and fill period of around three seconds is sufficient to fill the chamber with a fresh sample of decontaminant solution. The valve is then closed and the sample is held within the chamber for sufficient time to equilibrate the temperature and for the sampled fluid to become quiescent. Once this equilibration period is complete, a pulsed voltage sequence is applied to the electrodes, resulting in the generation of an electrical current which is correlated to the concentration of peracetic acid in the sample. The sampling and measurement steps are repeated, preferably every one to two minutes, to ensure that the peracetic acid concentration does not drop below a minimum acceptable level.

[0043] With reference once more to FIGURE 2, the amperometric controller **112** includes a voltage regulator **180** which applies a reference voltage (relative to the potential generated by the reference electrode) between the reference electrode **120** and the working electrode **118** of the embodiment of either FIGURE 3 or FIGURES 4 and 5. A voltage pulser **182** superimposes a read voltage between the reference and working electrodes in short pulses. The current flowing through the counter electrode is the same as that of the working electrode.

[0044] Since reference electrodes do not tend to conduct electricity well, this may lead to resistance problems. Additionally, the stability at the reference electrode may be compromised when large currents are drawn. It is desirable for the counter electrode **122** to be held at a potential sufficient to prevent current from flowing through the reference electrode. This is readily achieved by using one or more operational amplifiers 184, connected between the reference electrode 120 and counter electrode 122. The amplifiers only allow current to flow through the sampled solution between the working and the counter electrode. This allows precise control of the applied potential while blocking the reference electrode against carrying electrical current. The reference potential of the reference electrode is thus used to maintain/control the desired voltage potential applied between the working and reference electrodes so that the signal generated is well controlled.

[0045] The controller 112 also includes a current monitor 186 which detects the current flowing between the working and counter electrodes.

[0046] At a given temperature and voltage, the current measured is dependent on both the peracetic acid concentration and the concentration of other oxidizing species, such as hydrogen peroxide, in the solution tested. The respective contributions of each of these components to the overall current measured is dependent on the selected read voltage. Over a limited read voltage range, the hydrogen peroxide (or other oxidizing species present) has a much smaller influence on the current than the peracetic acid. Thus, by carefully selecting a read voltage which minimizes the effect of other oxidizing species, the current measured is virtually independent of the concentration of hydrogen peroxide and shows a linear relationship with peracetic acid concentration.

[0047] For solutions containing peracetic acid and hydrogen peroxide, the read voltage is preferably -0.5 to -1.4 volts, more preferably about -1.0 volts, relative to an Ag/AgCl reference electrode, when the working electrode and counter electrode are both carbon. Within this range, a preferred range for glassy carbon and iso-carbon is -0.9 to -1.1 volts and for pyrolytic graphite, -1.0 to -1.4 volts, more preferably, from -1.1 to -1.3 volts. The choice of range will also be partially dependent on pH, ionic strength, and temperature, the above ranges having been determined in near neutral solutions at temperatures of from about ambient to about 50°C.

[0048] To determine an appropriate read voltage a voltammetrac scan of the working electrode in both a peracetic acid-free solution (e.g. a buffer solution) is compared with a scan for the same solution but with peracetic acid present.

[0049] Before use, the working electrode may be treated to prepare the electrode surface for sensing. The pretreatment step improves the reproducibility of the electrode surface and consequently that of the sensed current. In the pretreatment step, gross debris tends to be removed from the surface of the electrode. Pretreatment of the electrode may be achieved by subsequent oxidation and reduction of the electrode surface by means of positive and negative pulses. This pretreatment step may be carried out in the reservoir 114 or in a separate vessel. The electrode is immersed in an electrolyte, such as a buffer solution or a sample of the decontaminant solution to be used. For example, sequential application of positive (+1.5 to +2.8V vs an Ag/AgCl reference electrode) and negative (-1.8 to -2.5 V vs the Ag/AgCl reference electrode) pulses (e.g., as a square or sine wave) of from about 1 to 8 seconds in duration are used. For example, about ten positive and negative

pulses are generally effective.

[0050] With reference now to FIGURE 6, a typical measurement sequence includes a preconditioning phase P and a read phase R. The preconditioning phase enhances the quality of the current signal received in the read phase, for example, by removing from the electrode components of the solution which have deposited on the electrode in prior measurement sequences. The precleaning step may also be used to ensure an optimal oxidation state of the electrode surface which catalyzes the detection process. A preferred preconditioning phase P includes applying a positive voltage pulse between the reference **122** and working electrode **118** (at about +1.2 to +2 volts vs Ag/AgCl, followed by a negative voltage pulse (of about -1.8 to -2.5 volts vs Ag/AgCl), each of the pulses lasting from about 1 to 8 seconds (i. e. a frequency of about 0.01Hz to 10 Hz, more preferably, 0.1 to 1 Hz). A sensing pulse at the read voltage (about -0.5 to -1.4 volts) is then applied for about 10 seconds.

[0051] The current flowing during the read pulse decays asymptotically to a fairly steady value. Preferably, the current is measured towards the end of the application of the read voltage when its value has substantially reached a steady state. For example, the current flowing during the last two to three seconds of the sensing pulse (the read phase) is measured and averaged to produce the signal that is used to measure the concentration of peracetic acid. This delays allows time for the discharging of capacitative currents and recharging of the double layer of the measurement electrode and establishment of a diffusion-limited current so that the current measured is derived from primarily faradaic reactions, rather than the primarily capacitative currents which occur during rapid voltage changes.

[0052] The pulse sequence of FIGURE 6 is repeated a plurality of times during the antimicrobial stage of the cycle, each time with a new sample of the circulated solution. Any residue build-up at the end of cycle is electrochemically removed at the beginning of the next cycle. More specifically, after the last measurement, liquid is retained in the electrolytic cell either by retaining the last sample or by filling the cell with rinse water in the subsequent rinse stage.

[0053] In the next cycle, the cell samples the solution after the buffers, wetting agents, and corrosion inhibitors have been circulated, but before the antimicrobial is added. With the sampled buffer solution, a series of voltage pulses are applied between the reference and working electrodes to drive off the residue, at a voltage about the voltage that causes hydrogen gas to form and below the voltage at which oxygen gas forms on the working electrode of the present configuration. The pulses are large enough to drive off the residue, but small enough that the carbon electrode is not electrochemically eroded. In the present system, alternating square wave pulses of +1.3 to +2.0 volts and - 1.8 to -2.5 volts are preferred. However, voltage pulses of -1.5 to -2.5 volt and +2.0 to +3.5 volts with durations of 1-10 seconds can also produce satisfactory results.

[0054] FIGURE 7 illustrates the relationship between voltage and current flow for solutions containing fixed concentrations of hydrogen peroxide and peracetic acid. The solutions tested were (1) a buffering system- to provide a "background" reading, (2) buffering system and 1500 ppm peracetic acid, and (3) buffering system and hydrogen peroxide and peroxide ions, for a pyrolytic graphite working electrode. It should be appreciated that some hydrogen peroxide was inevitably present in the peracetic acid sample due to the equilibrium concentration of hydrogen peroxide in peracetic acid. At the read voltage (around -0.5 to -1.4V for the system described above, relative to silver/silver chloride), the peracetic acid makes a much larger contribution to the current measured than the hydrogen peroxide present. Electrode systems **110** and applied voltages are readily designed which allow the contribution of peracetic acid to the current measured to be roughly ten times that of hydrogen peroxide, or greater. Unless the concentration of hydrogen peroxide in the solution to be tested is much greater than that of peracetic acid, the current output in the optimal read voltage range is, for all practical purposes, dependent on the peracetic acid concentration and almost independent of the hydrogen peroxide concentration.

[0055] In some instances the optimum read voltage may not be achievable in the electrochemical system due to background noise. At low voltages (about -20mV), the current output tends to be masked by background noise and therefore measurement of very low peracetic acid concentrations, in particular, may be difficult. Thus, the choice of a preferred read voltage is dependent on the likely concentrations of peracetic acid to be measured, the ratio of peracetic acid to hydrogen peroxide, and the degree of background noise in the system. Using a carbon electrode pushes the optimum read voltage away from the background noise region (-20mV). Read voltage pulses at about -0.5 to -1.4 volts relative to silver/silver chloride are ideal for detecting peracetic acid concentrations in the range of 100 ppm to 3000 ppm, when the hydrogen peroxide concentration is less than, or not substantially greater than, the peracetic acid concentration.

[0056] The choice of read voltage, within the preferred range, may also be selected to take advantage of a flat portion or plateau of the voltammogram, if one conveniently exists within the preferred range. Choosing a read voltage in a plateau region makes the current reading less sensitive to minor fluctuations in voltage.

[0057] The choice of materials for the electrodes thus affects the selection of a preferred read voltage. Other factors, such as temperature and pH, also influence the selection.

[0058] The current output increases with temperature. Preferably, the heated housing brings the temperature of the sample to a constant temperature for meas-

urements to be made.

[0059] Alternatively, where significant variations in temperature are anticipated, the detected current flows are preferably corrected for variations in the temperature. The thermistor **132**, in this embodiment, is placed in contact with the sample to be tested and measures the temperature of the peracetic acid sample. Current measurements are then compensated for variations in temperature. The computer control system **80** optionally corrects the detected current flows for variations in temperature detected by the thermistor **132**. The computer preferably accesses a look-up table **196** and determines the peracetic acid concentration corresponding to the current output measured. However, for automated processing systems where temperatures are controlled to within ± 0.5-1.0°C, the effect of temperature on the current is relatively small and thus temperature compensation may be unnecessary.

[0060] Preferably, the working electrode surface area is significantly smaller than that of the counter electrode. Thus, the current flow generated for a given peracetic acid concentration is limited by the working electrode surface area. The counter electrode has a larger surface area than the working electrode to avoid saturation of the electrode with electrons and a loss of the linear relationship between peracetic acid concentration and current flow at higher peracetic acid concentrations.

[0061] The read voltage is pulsed between the reference and working electrodes (and hence to the counter electrode) at a fixed rate. A preferred duration of read voltage is about 10 seconds. Because of double layer discharging and rate limiting diffusion effects, the current output decreases asymptotically with time, eventually reaching a plateau region in which the current output is relatively constant with time. A sample time of around 5-15 seconds allows such steady state conditions to be established. The controller **112** then detects the current output, from which the peracetic acid concentration is determined. Between each sampling period, the working electrode is preconditioned again, as described.

[0062] By repeating the sampling and the measurement of current output over a period of time, at intervals of about 30 seconds to two minutes, an accurate current measurement of the peracetic acid concentration in the sterilant solution or in the sample is obtained.

[0063] When peracetic acid is present in the sample, the working electrode becomes enriched with electrons when the sensing pulse is applied. This excess of electrons will tend to cause the peracetic acid molecules in the vicinity of the electrode to become reduced (i.e., accept electrons from the surface of the electrode.) The movement of electrons from the electrode into the solution via this mechanism produces the electrical current that can be measured.

[0064] The magnitude of the current produced is proportional to the concentration of the peracetic acid molecules close to the surface of the electrode. When the magnitude of the voltage is small (not negative enough), the rate at which the peracetic acid molecules react is slow compared to the rate at which the peracetic acid at the surface is replenished by diffusion from the bulk solution. As the voltage becomes more negative, the rate at which peracetic acid is consumed increases and, as time progresses, the concentration of peracetic acid close to the electrode is depleted. This results in the current dropping exponentially and asymptotically reaching a limit determined by the rate at which peracetic acid can diffuse from the bulk solution to the surface of the electrode (i.e., a diffusion limited current). The peracetic acid sensor A, as it is used herein, measures this diffusion limited current. The decontaminant solution contains a buffering system which acts as an electrolyte. When a voltage is applied, a small current will flow due to the electrical conductivity of the electrolyte. In addition, when chemical species are present that are susceptible to electrochemical conversion, an additional electrical current will be produced due to electrochemical conversions at the surfaces of the electrodes.

[0065] In one embodiment, the computer control system **80** signals an alarm **202** when the peracetic acid concentration of the bath drops below a preselected minimum peracetic acid concentration. Or, the computer adjusts the length of the cycle to compensate for a reduced peracetic acid concentration.

[0066] In another embodiment, the control system 80 adjusts the concentration of peracetic acid flowing through the system in response to the detected concentration. In this embodiment, the control system signals a valve **204** in fluid communication with the fluid line **60** to open and release an additional dose of the concentrated source of peracetic acid into the system from a supplementary dispenser, such as a reservoir **206**, or other source of the concentrate. Other means of adjusting the peracetic acid concentration are also contemplated.

[0067] Because the electrodes **118', 120', 122'** in the reusable sensor **A'** tend to degrade over time, they should be replaced at intervals to maintain the accuracy of the sensor. Optionally, a calibration check is carried out prior to a sterilization cycle with a peracetic acid containing solution or solutions of known concentration, preferably concentrations in the range to be measured. The reference electrode **120'** may be checked every decontaminant cycle by measuring the magnitude of the reference potential relative to the carbon electrodes **118', 120'** and/or the stainless steel housing in the presence of an electrolyte. The electrolyte may be the pretreatment mixture of buffers, corrosion inhibitors, and the like, which is circulated through the system prior to addition of the peracetic acid decontaminant.

[0068] It is also important to maintain the surface condition of the working electrode, since the active area of the working electrode affects the magnitude of the measured current. conductivity measurement may be made periodically to provide information on the state of the electrode surface. For example, the conductivity is

measured each cycle in the presence of the buffers and corrosion inhibitors. Provided that the ionic strength of the buffered solution does not vary significantly from cycle to cycle, the conductivity measurements can be used to provide an indication of the state of the working electrode surface. Theoretically, the electrical resistance between the housing and the working electrode is a function on both the surface area of the housing and the surface area of the working electrode. Since the surface area of the housing is significantly larger than that of the working electrode, the electrical resistance will be more sensitive to changes in surface area of the working electrode.

[0069] When the electrodes **118', 120', 122'** are to be reused, it is preferable to maintain the working surfaces in contact with an electrolyte or water between decontaminant cycles. Accordingly, a sample of the decontaminant solution is left in the chamber at the end of a cycle. Or, the chamber is filled with a fresh solution of electrolyte or rinse water. particularly when the system 1 is not to be used for some time, the electrodes may be removed from the sensor **A'** and stored in an electrolyte solution or water until needed.

[0070] In an alternative embodiment, one or more of the electrodes is disposable, while the remaining are reusable. For example, a card type sensor **125** of the type shown in FIGURE 3 may be used for the working and counter electrodes **118, 122** in combination with a reusable reference electrode **120'** of the type shown in FIGURES 4 and 5. The card is disposed after a decontamination cycle, and the reference. electrode **120'** is reused.

[0071] It will be appreciated that the peracetic acid monitoring system **A, A'** may also be used in a variety of other peracetic acid sterilization/ disinfection systems in which items to be microbially decontaminated are immersed in, or sprayed with a peracetic acid solution. The system may also be used to detect the concentration of peracetic acid in a bath containing peracetic acid or in fluid flow lines of a water treatment system, bleaching plant, or similar system. Where the solution to be tested does not act as an electrolyte, an electrolyte may be added to the sample to be analyzed prior to making measurements.

[0072] While the system has been described with particular reference to detection of peracetic acid, the system is also applicable to detection of hydrogen peroxide and other oxidizing species. For example, other peracids, or mixtures of peracids are also useful antimicrobial agents.

[0073] Without intending to limit the scope of the invention, the following examples show cyclic voltammograms for carbon electrodes at differing peracetic acid concentrations.

EXAMPLES

[0074] Cyclic voltammograms were performed on glassy carbon and pyrolytic graphite working electrodes in solutions at different peracetic acid levels. FIGURES 8 and 9 show exemplary voltammograms for glassy carbon and pyrolytic graphite, respectively. For both these electrode materials, there is a plateau region in which the current remains relatively stable. This plateau region overlaps the voltage range in which the electrode shows greater sensitivity to peracetic acid than to hydrogen peroxide.

Claims

1. A method of measuring peracetic acid in a solution which also contains hydrogen peroxide, the method comprising disposing:

   (a) a carbon working electrode (118) and a reference electrode (120), or
   (b) a carbon working electrode (118), a reference electrode (120), and a counter electrode (122),

   in the solution to be tested, selectively applying a read voltage to the working electrode, detecting current flowing between either the working electrode and the reference electrode or the working electrode and the counter electrode (122); where present, and converting the detected current flow into an indication of the concentration of the peracetic acid in the solution the method **characterized by:**

   selectively pulsing the read voltage to the working electrode;
   the read voltage being selected such that the current flowing is dependent on a concentration of the peracetic acid and substantially independent of a concentration of the hydrogen peroxide in the solution, the read voltage being in the range of -0.5 to -1.4 volts, relative to a silver/ silver chloride reference electrode.

2. The method of claim 1, further **characterized by:**

   the read voltage being selected such that a contribution of the peracetic acid to the current flowing is at least ten times that of an equivalent concentration of the hydrogen peroxide.

3. The method of either one of preceding claims 1 and 2, further **characterized by the** read voltage being in the diffusion limiting range.

4. The method of any one of preceding claims 1-3, further **characterized by:**

   the read voltage being selected to provide a

high signal to noise ratio.

5. The method of any one of preceding claims 1-4, further **characterized by**:

the read voltage being selected to be within a voltammetric plateau region where current is relatively insensitive to minor changes in read voltage.

6. The method of any one of preceding claims 1-5, further **characterized by**:

the working electrode being formed from pyrolytic graphite and the read voltage being in the range of -1.1 to -1.3 volts, relative to a silver/silver chloride reference electrode.

7. The method of any one of preceding claims 1-6, further **characterized by**:

the peracetic acid concentration being in the range of 100 to 3000 ppm.

8. The method of claim 7, further **characterized by**:

the peracetic acid concentration being determined in under one minute.

9. The method of any one of preceding claims 1-8, further **characterized by**:

the selective application of the read voltage and the detection of the current flowing are repeated at intervals of from about ten to thirty seconds.

10. The method of any one of preceding claims 1-9, further **characterized by**:

prior to the step of applying the read voltage:

conditioning the working electrode by applying at least one positive pulse and applying at least one negative pulse to the electrode.

11. The method of any one of preceding claims 1-10, further **characterized by**:

detecting a temperature of the solution adjacent the electrodes; and
correcting the detected current flowing for a difference between the detected temperature and a preselected temperature.

12. The method of any one of preceding claims 1-11, further **characterized by**:

increasing the peracetic acid concentration in the solution when the concentration is below a preselected minimum level.

13. The method of any one of preceding claims 1-12, further **characterized by**:

prior to the step of disposing a working electrode and a reference electrode in the solution to be tested:

circulating the solution though a treatment vessel (12) which contains items to be decontaminated; and

the step of disposing the working electrode, reference electrode, and counter electrode, where present, in the solution to be tested including:

withdrawing a sample of the circulated solution into a chamber (114) to contact the electrodes.

14. The method of claim 13, further **characterized by**:

prior to the step of circulating the solution though the treatment vessel:

circulation a preconditioning solution including buffers and wetting agents though the treatment vessel; and
withdrawing a sample of the preconditioning solution into the chamber; and

pulsing voltages between the reference and working electrodes which electrochemically remove residues from the working electrode.

15. The method of either one of preceding claims 13 and 14, further **characterized by**:

prior to the step of withdrawing a sample of the circulated solution into a chamber:

filling the chamber with solution; and
emptying solution from the chamber to flush residue from previous measurements from the chamber.

16. The method of any one of preceding claims 13-15, further **characterized by**:

signaling an indication of the current measured to a control system (80), which, in the event that the current measured is below a predetermined minimum level, conducts at least one of the following steps:

aborting the decontamination process;
extending the time of the decontamination process to compensate for the peracetic acid concentration;
controlling the addition of additional peracetic acid to the circulating solution; and
providing a signal which indicates that the peracetic acid concentration is below the predetermined minimum level.

Patentansprüche

1. Eine Methode zur Messung der Konzentration von Peressigsäure in einer, unter anderem, Wasserstoffperoxid enthaltenden Lösung, und die Methode daraus besteht, dass

   (a) eine Kohlenstoff-Arbeitselektrode (118) und eine Referenzelektrode (120) oder

   (b) eine Kohlenstoff-Arbeitselektrode (118), eine Referenzelektrode (120) und eine Zählelektrode (122)

   in die zu messende Lösung eingebracht werden, dass eine Mess-Spannung an der Arbeitselektrode angelegt und entweder der zwischen der Arbeitselektrode und der Referenzelektrode oder zwischen der Arbeitselektrode und, sofern vorhanden, der Zählelektrode (122) fließende Strom gemessen wird und dass ein Konvertierung des gemessenen Stroms in eine Anzeige für die Peressigsäure-Konzentration der Lösung erfolgt, wobei die Methode **dadurch gekennzeichnet ist, dass:**

   die an die Arbeitselektrode angelegte Mess-Spannung gezielt pulsiert wird;

   die Mess-Spannung so gewählt wird, dass der daraufhin fließende Strom abhängig ist von einer Konzentration der Peressigsäure und im Wesentlichen unabhängig von der Konzentration des Wasserstoffperoxids in der Lösung, wobei die Mess-Spannung in einem Bereich von -0,5 bis -1,4 Volt relativ zu einer Silber/Silberchlorid-Referenzelektrode liegt.

2. Die Methode gemäß Anspruch 1, des weiteren **dadurch gekennzeichnet, dass**
   die Mess-Spannung so gewählt wird, das der Anteil des auf Grund der Peressigsäure fließenden Stroms wenigstens zehnmal so hoch ist wie der bei einer vergleichbaren Konzentration des Wasserstoffperoxids.

3. Die Methode gemäß eines beliebigen der vorhergehenden Ansprüche 1 und 2 und des weiteren **dadurch gekennzeichnet, dass**
   die Mess-Spannung in dem Bereich liegt, wo nur eine geringe Diffusion an der Elektrode stattfindet..

4. Die Methode gemäß eines beliebigen der vorhergehenden Ansprüche 1 bis 3 und des weiteren **dadurch gekennzeichnet, dass**
   die Mess-Spannung so gewählt wird, dass ein hoher Rauschabstand erzielt wird.

5. Die Methode gemäß eines beliebigen der vorhergehenden Ansprüche 1 bis 4 und des weiteren **dadurch gekennzeichnet, dass**
   die Mess-Spannung so gewählt wird, dass sie im Bereich eines Strom/Spannungsplateaus liegt, wo also der Strom relativ unempfindlich ist gegenüber kleineren Schwankungen der Mess-Spannung.

6. Die Methode gemäß eines beliebigen der vorhergehenden Ansprüche 1 bis 5 und des weiteren **dadurch gekennzeichnet, dass**
   die Arbeitselektrode aus pyrolytischem Graphit besteht und die Mess-Spannung in dem Bereich zwischen -1,1 und -1,3 Volt relativ zu einer Silber/Silberchlorid-Referenzelektrode liegt.

7. Die Methode gemäß eines beliebigen der vorhergehenden Ansprüche 1 bis 6 und des weiteren **dadurch gekennzeichnet, dass**
   die Konzentration der Peressigsäure in dem Bereich zwischen 100 und 3000 ppm liegt.

8. Die Methode gemäß Anspruch 7, des weiteren **dadurch gekennzeichnet, dass**
   die Konzentration der Peressigsäure in weniger als einer Minute bestimmt werden kann.

9. Die Methode gemäß eines beliebigen der vorhergehenden Ansprüche 1 bis 8 und des weiteren **dadurch gekennzeichnet, dass**
   das gezielte Anlegen der Mess-Spannung und die Messung des Stroms in Intervallen von ungefähr zehn bis dreißig Sekunden wiederholt wird.

10. Die Methode gemäß eines beliebigen der vorhergehenden Ansprüche 1 bis 9 und des weiteren **dadurch gekennzeichnet, dass**
    vor dem Anlegen der Mess-Spannung,
    die Arbeitselektrode konditioniert wird
    und zwar durch Anlegen zumindest eines positiven Spannungspulses und durch Anlegen zumindest eines negativen Spannungspulses an die Elektrode.

11. Die Methode gemäß eines beliebigen der vorhergehenden Ansprüche 1 bis 10 und des weiteren **dadurch gekennzeichnet, dass**

die Temperatur der Lösung in direkter Nähe der Elektroden gemessen wird; und

Der Messwert des Stroms hinsichtlich der Differenz zwischen gemessener Temperatur und einer vorher spezifizierten Temperatur korrigiert wird.

12. Die Methode gemäß eines beliebigen der vorhergehenden Ansprüche 1 bis 11 und des weiteren **dadurch gekennzeichnet, dass**

die Konzentration der Peressigsäure in der Lösung erhöht wird, sobald die Konzentration unter einen vorher spezifizierten Wert fällt.

13. Die Methode gemäß eines beliebigen der vorhergehenden Ansprüche 1 bis 12, des weiteren **dadurch gekennzeichnet, dass**

vor dem Schritt des Eintauchens einer Arbeitselektrode und einer Referenzelektrode in die zu prüfende Lösung,

die Lösung durch einen Behandlungsbehälter (12), in dem sich die zu dekontaminierenden Gegenstände befinden, zirkuliert wird; und

der Schritt des Eintauchens der Arbeitselektrode, der Referenzelektrode und, sofern vorhanden, der Zählelektrode in die zu prüfende Lösung auch umfasst,

dass der zirkulierenden Lösung eine Probe entnommen und diese in eine Kammer (114) umgefüllt wird und damit die Benetzung der Elektroden erfolgt.

14. Die Methode gemäß Anspruch 13, des weiteren **dadurch gekennzeichnet, dass**

vor dem Schritt des Zirkulierens der Lösung durch den Behandlungsbehälter

eine Vorkonditionierungs-Lösung einschließlich Puffer und Netzmittel durch den Behandlungsbehälter gepumpt wird; und

der Vorkonditionierungs-Lösung eine Probe entnommen und in die Kammer gefüllt wird; und

eine pulsierende Spannung zwischen Referenz- und Arbeitselektrode angelegt wird, um somit Rückstände von der Arbeitselektrode zu entfernen.

15. Die Methode gemäß eines beliebigen der vorhergehenden Ansprüche 13 und 14 und des weiteren **dadurch gekennzeichnet, dass**

vor dem Schritt der Entnahme einer Probe aus der zirkulierenden Lösung und Umfüllen dieser Probe in eine Kammer

die Kammer mit Lösung gefüllt wird; und

die Lösung aus der Kammer entleert wird, um somit Rückstände von vorherigen Messungen aus der Kammer zu entfernen.

16. Die Methode gemäß eines beliebigen der vorhergehenden Ansprüche 13 bis 15 und des weiteren **dadurch gekennzeichnet, dass**

der Messwert des Stroms an ein Regelsystem (80) übertragen wird, das zumindest eines der folgenden Schritte ausführt, wenn der gemessene Strom unter einem vorher spezifizierten Mindestwert liegt:

Abrechen des Dekontaminationsvorgangs;

Verlängern des Dekontaminationsvorgangs als Kompensation für die geringere Konzentration der Peressigsäure;

Steuerung der Zufuhr von zusätzlicher Peressigsäure in die zirkulierende Lösung; und

Ausgabe eines Signals, mit dem angezeigt wird, dass die Konzentration der Peressigsäure unter einem vorher spezifizierten Mindestwert liegt.

Revendications

1. Procédé de mesure d'acide peracétique dans une solution qui contient également du peroxyde d'hydrogène, le procédé comprenant les étapes consistant à déposer :

(a) une électrode de travail au carbone (118) et une électrode de référence (120), ou
(b) une électrode de travail au carbone (118), une électrode de référence (120), et une contre-électrode (122),

dans la solution à analyser, à appliquer de manière sélective une tension électrique de lecture à l'électrode de travail, à détecter du courant circulant entre l'électrode de travail et l'électrode de référence ou l'électrode de travail et la contre-électrode (122), si elles sont présentes, et à convertir l'écoulement de courant détecté en une indication de la concentration d'acide peracétique dans la solution, le procédé étant **caractérisé en ce que** :

la tension électrique de lecture est appliquée par impulsions de manière sélective vers l'électrode de travail ;
la tension de lecture étant sélectionnée de sorte que le courant s'écoulant soit dépendant d'une concentration de l'acide peracétique et sensiblement indépendant d'une concentration du peroxyde d'hydrogène dans la solution, la tension électrique de lecture étant comprise dans la plage allant de -0,5 à -1,4 volts, par rapport à une électrode de référence argent/chlorure d'argent.

2. Procédé selon la revendication 1, **caractérisé, en outre, en ce que** la tension électrique de lecture est sélectionnée de sorte qu'une contribution de l'acide peracétique au courant en circulation soit au moins égale à dix fois celle d'une concentration du peroxyde d'hydrogène.

3. Procédé selon l'une quelconque des revendications précédentes 1 et 2, **caractérisé, en outre, en ce que** la tension électrique de lecture se situe dans la plage limite de diffusion.

4. Procédé selon l'une quelconque des revendications précédentes 1 à 3, **caractérisé, en outre, en ce que** la tension électrique de lecture est sélectionnée pour fournir un rapport signal à bruit élevé.

5. Procédé selon l'une quelconque des revendications précédentes 1 à 4, **caractérisé, en outre, en ce que** la tension électrique de lecture est sélectionnée pour être dans une région du plateau de voltampères où le courant est relativement insensible aux changements mineurs de la tension électrique de lecture.

6. Procédé selon l'une quelconque des revendications précédentes 1 à 5, **caractérisé, en outre, en ce que** l'électrode de travail est formée avec du graphite pyrolytique et la tension électrique de lecture est comprise dans la plage allant de -1,1 à -1,3 volts, par rapport à une électrode de référence argent/chlorure d'argent.

7. Procédé selon l'une quelconque des revendications précédentes 1 à 6, **caractérisé, en outre, en ce que** la concentration d'acide peracétique est comprise dans la plage allant de 100 à 3000 ppm.

8. Procédé selon la revendication 7, **caractérisé, en outre, en ce que** la concentration d'acide peracétique est déterminée en moins d'une minute.

9. Procédé selon l'une quelconque des revendications précédentes 1 à 8, **caractérisé, en outre, en ce que** l'application sélective de la tension électrique de lecture et la détection du courant en circulation sont répétées à des intervalles allant d'environ dix à trente secondes.

10. Procédé selon l'une quelconque des revendications précédentes 1 à 9, **caractérisé, en outre, en ce que**, avant l'étape consistant à appliquer la tension électrique de lecture, l'électrode de travail est conditionnée en appliquant au moins une impulsion positive et au moins une impulsion négative à l'électrode.

11. Procédé selon l'une quelconque des revendications précédentes 1 à 10, **caractérisé, en outre,** par :

la détection d'une température de la solution au voisinage des électrodes ; et
la correction du courant en circulation détecté en vue d'une différence entre la température détectée et une température présélectionnée.

12. Procédé selon l'une quelconque des revendications précédentes 1 à 11, **caractérisé, en outre,** par :

l'augmentation de la concentration d'acide peracétique dans la solution lorsque la concentration est inférieure à un niveau minimum présélectionné.

13. Procédé selon l'une quelconque des revendications précédentes 1 à 12, **caractérisé, en outre, en ce que**, avant l'étape consistant à disposer une électrode de travail et une électrode de référence dans la solution à analyser, on fait circuler la solution à travers un récipient de traitement (12) qui contient des articles à décontaminer ; et
l'étape consistant à disposer l'électrode de travail, l'électrode de référence, et la contre-électrode, si elles sont présentes, dans la solution à analyser comprenant :

le prélèvement d'un échantillon de la solution que l'on fait circuler dans une chambre (114) pour le contact des électrodes.

14. Procédé selon la revendication 13, **caractérisé, en outre, en ce que** avant l'étape consistant à faire circuler la solution à travers le récipient de traitement, on fait circuler une solution de préconditionnement comprenant des tampons et des agents mouillants à travers le récipient de traitement ; un échantillon de la solution préconditionnée à l'intérieur de la chambre est prélevé ; et des tensions électriques sont appliquées par impulsions entre les électrodes de référence et les électrodes de travail qui suppriment électrochimiquement les résidus de l'électrode de travail.

15. Procédé selon l'une quelconque des revendications précédentes 13 et 14, **caractérisé, en outre, en ce que**, avant l'étape consistant à prélever un échantillon de la solution que l'on fait circuler à l'intérieur d'une chambre, on remplit la chambre avec la solution ; et on évacue la solution hors de la chambre pour faire écouler le résidu des précédentes mesures hors de la chambre.

16. Procédé selon l'une quelconque des revendications précédentes 13 et 15, **caractérisé, en outre,** par :

le signalement d'une indication du courant me-

suré à un système de contrôle (80), qui, au cas où le courant mesuré est inférieur à un niveau minimum prédéterminé, assure au moins l'une des étapes suivantes :

provoquer l'arrêt du processus de décontamination ;
allonger le temps du processus de décontamination pour compenser la concentration d'acide peracétique ;
contrôler l'ajout d'acide peracétique supplémentaire à la solution en circulation ; et fournir un signal qui indique que la concentration d'acide peracétique est inférieure au niveau minimum prédéterminé.

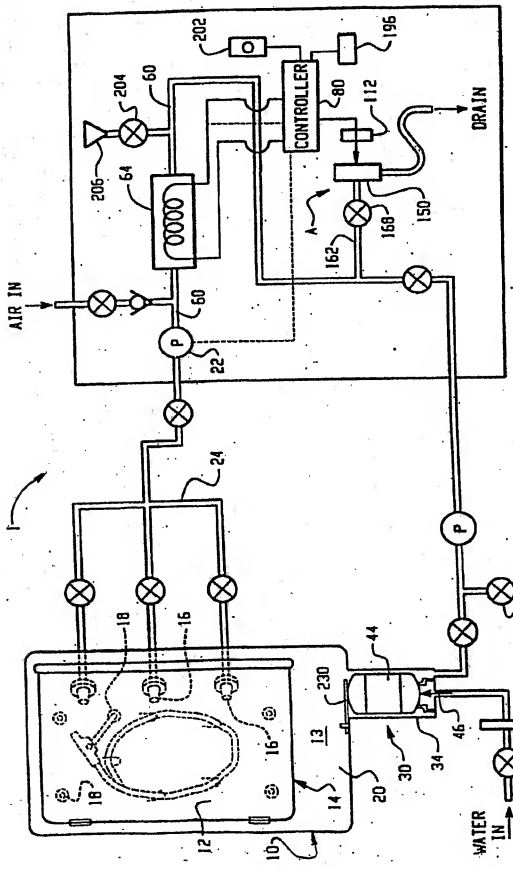
AIR IN
DRAIN
CONTROLLER
WATER IN
DRAIN
10
12
13
14
16
18
20
22
24
30
34
42
44
46
50
52
60
64
80
112
150
162
168
195
196
202
204
206
230
240
A

Fig. 1

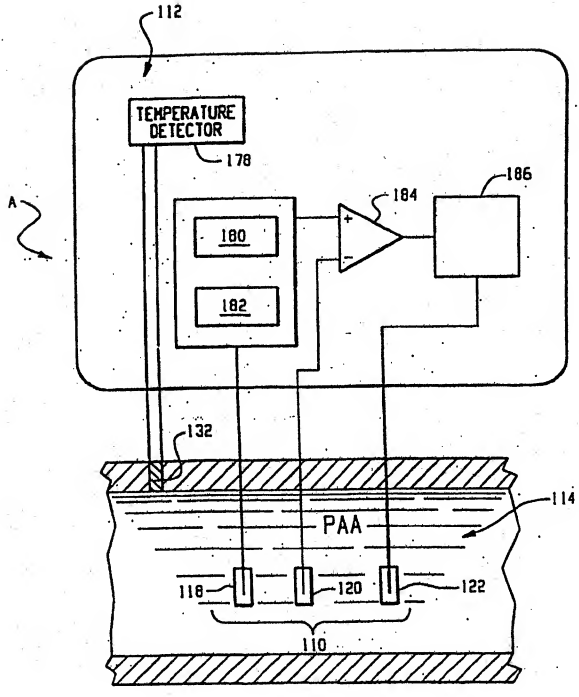
112
TEMPERATURE DETECTOR
178
A
180
182
184
186
132
114
PAA
118
120
122
110

Fig. 2

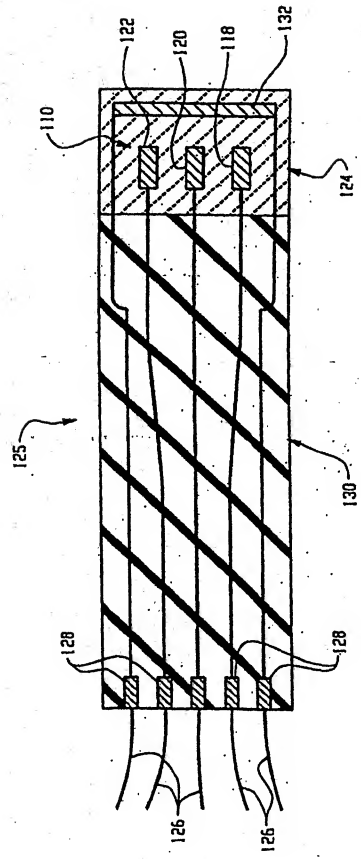

Fig. 3

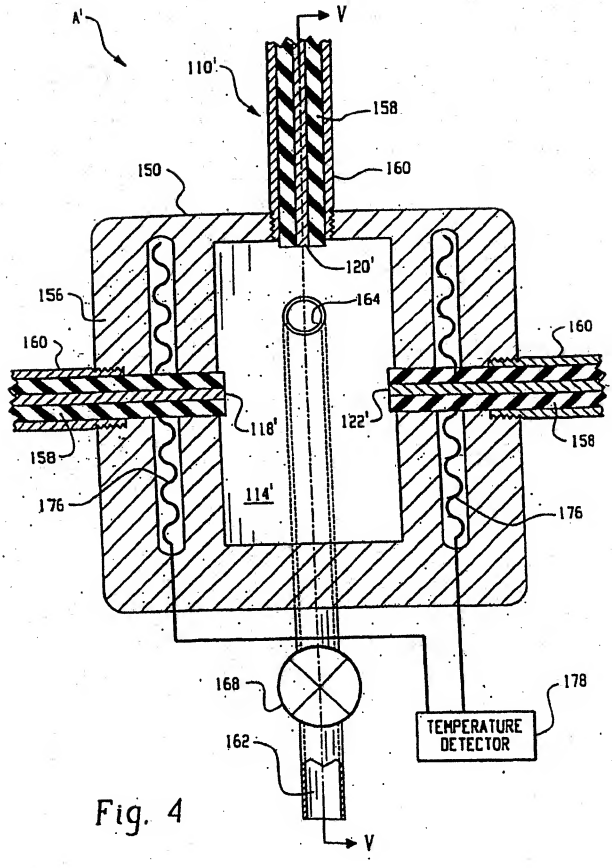
A'
V
110'
158
160
150
120'
156
164
160
160
118'
122'
158
158
176
114'
176
168
178
TEMPERATURE DETECTOR
162
V

Fig. 4

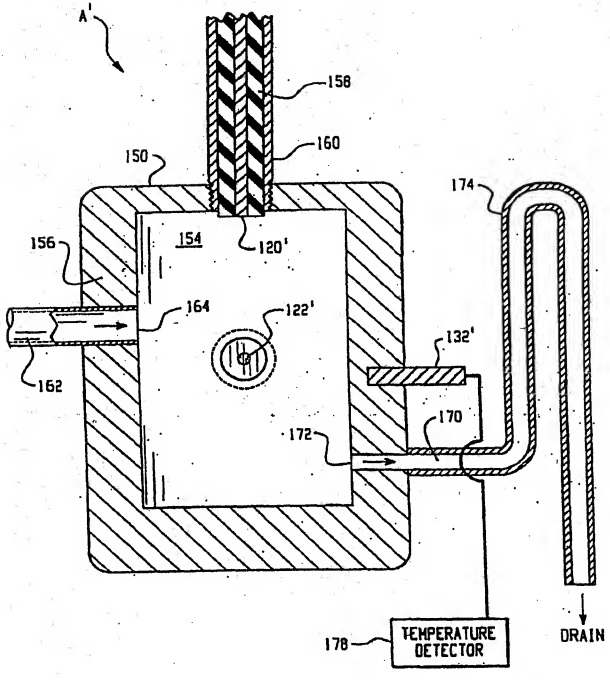
A'
158
160
150
174
156
154
120'
164
122'
132'
162
170
172
178
TEMPERATURE DETECTOR
DRAIN

Fig. 5

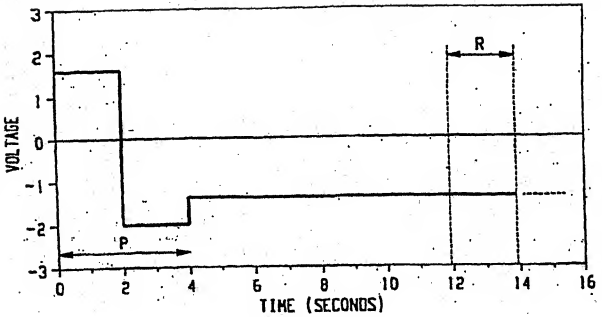

Fig. 6

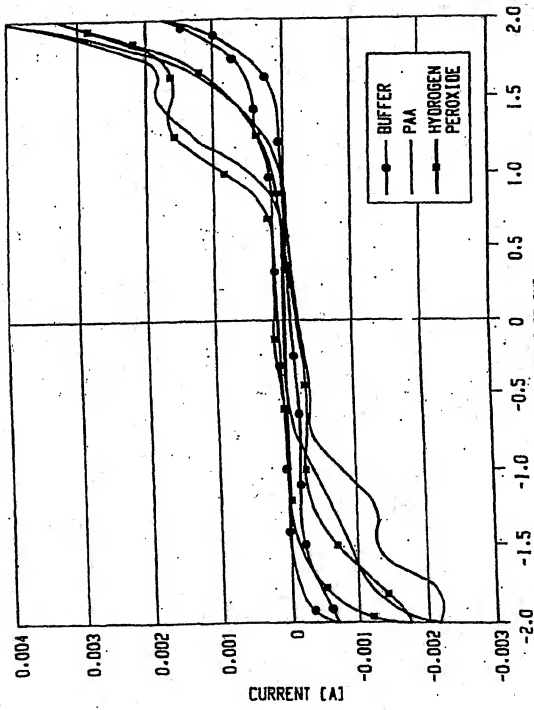
BUFFER
PAA
HYDROGEN PEROXIDE
CURRENT [A]
VOLTAGE [V]
0.004
0.003
0.002
0.001
0
-0.001
-0.002
-0.003
2.0
1.5
1.0
0.5
0
-0.5
-1.0
-1.5
-2.0

Fig. 7

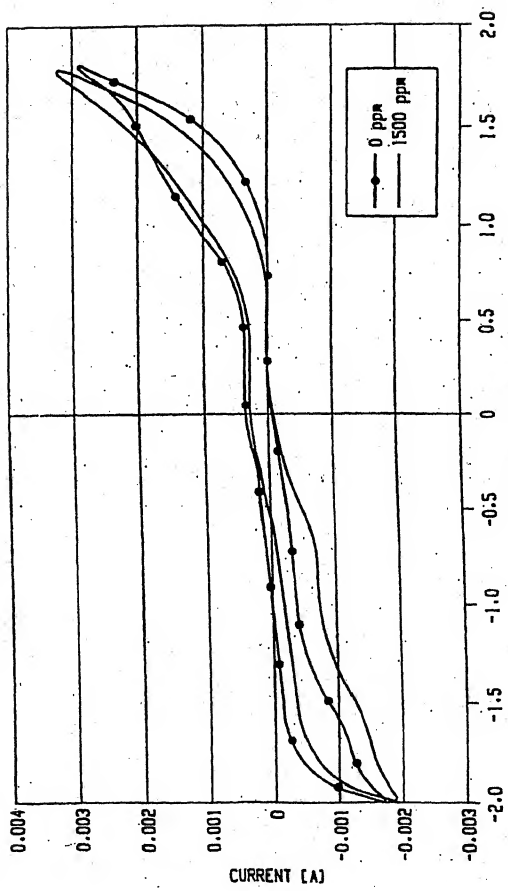
0.004
0.003
0.002
0.001
0
-0.001
-0.002
-0.003
CURRENT [A]
-2.0
-1.5
-1.0
-0.5
0
0.5
1.0
1.5
2.0
VOLTAGE (vs. Ag/AgCl)
0 ppm
1500 ppm

Fig. 8

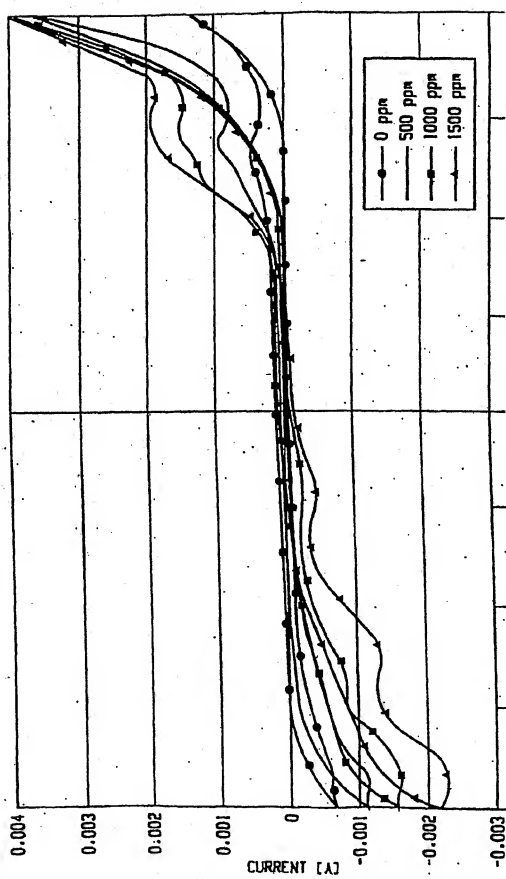
0.004
0.003
0.002
0.001
0
-0.001
-0.002
-0.003
CURRENT [A]
-2.0
-1.5
-1.0
-0.5
0
0.5
1.0
1.5
2.0
VOLTAGE (vs. Ag/AgCl)
0 ppm
500 ppm
1000 ppm
1500 ppm

Fig. 9